# **Chapter 4**



## **Ozone Concentrations**

Hubbard Brook, New Hampshire (WST109)

CASTNet is considered the principal source of information on rural  $O_3$  concentrations in the United States. CASTNet  $O_3$  data provide information on geographic patterns in regional  $O_3$  and on the extent to which rural areas potentially exceed the concentration levels mandated by the NAAQS. Measurements of 1-hour and 8-hour concentrations and SUM06 levels during 2001 are about the same as 2000 but lower than 1999. Over the period 1990 through 2001, three to five sites typically experienced 1-hour concentrations above 125 parts per billion (ppb). Approximately 35 to 50 percent of CASTNet sites measured fourth highest daily maximum 8-hour  $O_3$  levels above 85 ppb. No trend was evident in the measurements.

Ozone concentrations were measured continuously at 77 CASTNet sites during 2001. Based on the CASTNet siting criteria, the O<sub>3</sub> measurements are generally considered regionally representative and, therefore, able to define geographic patterns of rural ozone across most of the United States. CASTNet is considered the nation's primary source of information on rural O<sub>3</sub> levels.

Ozone measurements are obtained from both EPA and NPS sponsored CASTNet sites. CASTNet QA procedures for EPA O<sub>3</sub> analyzers are different from SLAMS procedures. On the other hand, the NPS O<sub>3</sub> operations meet the SLAMS requirements. Consequently, not all of the O<sub>3</sub> data can be used to gauge compliance with ozone NAAQS. However, all of these data are appropriate for use in establishing general status and trend patterns in regional O<sub>3</sub> levels and for making general

statements regarding the extent to which rural areas potentially exceed the concentration levels mandated by the NAAQS.

This chapter provides information on hourly and 8-hour O<sub>3</sub> concentrations and SUM06 values collected during 2001 and trends over the 12-year period 1990 through 2001. Meteorological measurements taken in 2001 and over the 12-year period are analyzed to provide perspective to the O<sub>3</sub> data.

#### **One-Hour Concentrations**

Figure 4-1 presents the second highest daily maximum 1-hour values for 2001. The shading indicates two regions of elevated hourly O<sub>3</sub> levels extending from Maryland along the coast to southern Maine and also in California. Washington's Crossing, NJ (WSP144) and

Abington, CT (ABT147) are the two sites that measured second highest daily maximum 1-hour O<sub>3</sub> concentrations above 125 ppb during 2001.

CASTNet O<sub>3</sub> data provide information on geographic patterns of rural ozone across most of the United States. Over the period 1990 through 2001, three to five sites typically measured 1-hour concentrations above 125 ppb. Approximately 35 to 50 percent of CASTNet sites measured fourth highest daily maximum 8-hour O<sub>3</sub> levels above 85 ppb. No trends were evident in the measurements. CASTNet O<sub>3</sub> data exhibited significant interannual variability in the magnitude and extent of high concentrations that was related to the variability in meteorological conditions.

### **Eight-Hour Concentrations**

The fourth highest daily maximum 8-hour average O<sub>3</sub> concentrations measured during 2001 are presented in Figure 4-2. Fifteen eastern and two California sites measured concentrations above 85 ppb. The region with the highest 8-hour levels extended from Virginia northward to southeastern Maine including a narrow band in New England from ABT147 to ACA416. Other locations in the eastern United States that observed 8-hour O<sub>3</sub> levels above 85 ppb included sites in western Pennsylvania, eastern Ohio, Michigan, and the site at Great Smoky Mountains National Park, TN (GRS420). The two sites in the western United States that observed 8-hour O<sub>3</sub> levels above 85 ppb were both located in California: Sequoia National Park (SEK402) and Yosemite National Park (YOS404). Three sites in the network (SEK402, ABT147, and WSP144) observed values above 100 ppb. The geographic extent of the high 8-hour concentrations in 2001 was about the same as was observed in 2000. The lowest daily maximum 8-hour concentrations in the continental United States were observed in the Northwest, with the lowest value of 45 ppb measured at OLY421.

#### SUM<sub>06</sub>

SUM06 is calculated as the sum of hourly O<sub>3</sub> concentrations above 0.06 parts per million (ppm) summed over 12 hours (0800 to 2000) during a 3-month period. A map of peak SUM06 values for 2001 is given in Figure 4-3. The peak values were taken as the maximum rolling 3-month SUM06 at each CASTNet site. Eighteen eastern and three California sites had values above 25 ppm-hours (ppm-hr). The geographic extent and magnitude of high values were relatively low in 2001 - lower than 2000 and much lower than 1999. During 2001, observed SUM06 values increased in a region in the eastern United States extending from Illinois and Wisconsin eastward into New England. The majority of sites in the southern tier of the eastern United States and all but seven western sites observed decreases. Several sites in the network recorded SUM06 values less than 1.0 ppm-hr, including sites in North Dakota, Montana, and Washington and also at sites in Alaska, Hawaii, and the Virgin Islands.

SUM06 is a measure of vegetation and crop exposure to ozone during the growing season. The geographic extent and magnitude of high SUM06 values were relatively low in 2001. All but seven western sites recorded decreases in SUM06 in 2001 versus 2000 despite warmer, sunnier, and drier weather in the west during the ozone season. Three sites in California recorded the highest SUM06 values during 2001.

### **Ozone Flux**

Figure 4-4 presents a map of modeled 2001 ozone fluxes. These estimates represent the dry deposition of O<sub>3</sub> to the environment. The highest fluxes were estimated for the Virginias, Kentucky, and North Carolina. The peak value (74.7 kg/ha/yr) was modeled at GRS420. The modeled flux estimates are approximately correlated with annual mean O<sub>3</sub> deposition velocities (see Appendix C).

#### **Twelve-Year Trends**

The 12-year trend in the second highest daily maximum 1-hour O<sub>3</sub> concentrations is provided in Figure 4-5. The box plot was constructed using the 34-station subset of data used in all the trend analyses. The figure shows that 2001 observed relatively low 1-hour concentrations, with a median value less than the median measured in 2000. Figure 4-6 provides a box plot of fourth highest daily maximum 8-hour average O<sub>3</sub> concentrations. The 2001 8-hour values are similar to 2000 values. The trend in SUM06 is provided in Figure 4-7. The figure shows slightly higher SUM06 values in 2001 relative to 2000. This result is somewhat inconsistent in that the measured peak SUM06 values for 2001 (Figure 4-3) are lower than the same measurements for 2000. The explanation involves the mean value for the 34-station subset of reference sites versus the mean value for all stations in the network. The mean of the peak SUM06 values for the 34-station subset for 2001 is 22.4 ppm-hr, which is higher than the mean value of 20.9 ppm-hr for the same sites for 2000. In contrast, the mean of the peak values measured for all sites in 2001 is 19.7 ppm-hr, which is lower than the 2000 mean value of 21.4 ppm-hr.

Twelve-year trends in temperature, solar radiation, and precipitation measurements from the 34 eastern reference sites were analyzed to provide perspective to the box plots of the three sets of O<sub>3</sub> parameters. Measurements taken over the period May though September were analyzed. All hourly temperature and solar radiation values were averaged by site. All precipitation amounts were summed. Figures 4-8 through 4-10 present box plots of temperature, solar radiation, and precipitation measurements over the 12 years. The relationship between O<sub>3</sub> concentrations and the three meteorological parameters is shown by comparison of the six box

plots (Figures 4-5 through 4-10). Relatively low O<sub>3</sub> concentrations were observed during cool, cloudy years (e.g., 1992 and 2000); relatively high concentrations were measured during warm, sunny years (e.g., 1991 and 1999). The year 2001 is somewhat of an anomaly in that O<sub>3</sub> concentrations remained at about 2000 levels even though the mean solar radiation value increased significantly and precipitation decreased. The mean temperature remained relatively cool.

# Geographic Distribution of Differences in Meteorological Parameters

Maps of differences between 2001 seasonal and 6-year (1995-2000) seasonal temperature, solar radiation, and precipitation values were prepared to illustrate further the geographic distribution of O<sub>3</sub> concentrations. To provide a "climatological" value, all valid hourly temperature and solar radiation measurements collected over the period May through September were averaged over the six years 1995 through 2000. Precipitation amounts were summed. Seventy percent data completeness was required for all site-years. Additionally, an annual value for five of the six years was required. 2001 values were calculated separately. The sixyear climatological values were subtracted from the 2001 values. These differences were plotted on three maps for temperature, solar radiation, and precipitation (Figures 4-11 through 4-13, respectively). Data were available for 67 sites. Positive values indicate that 2001 had higher values (e.g., more solar radiation) than the six-year period.

Figure 4-11 shows cooler temperatures were observed at CASTNet sites located throughout most of the eastern United States during the 2001 ozone season. However, warmer temperatures were observed from eastern Pennsylvania northward through New England and also in southern Illinois, Indiana, and at the majority of the northernmost

sites. Most of the western sites observed warmer temperatures.

A map of differences in solar radiation is provided in Figure 4-12. The map shows CASTNet sites with above-normal solar radiation during 2001 along the east coast from North Carolina to New England and also in Illinois and southern Indiana into Kentucky. Most of the western CASTNet sites measured higher solar radiation values.

Precipitation differences for 2001 are shown in Figure 4-13. An area with above-normal precipitation extends from eastern Tennessee to southern New England. Other eastern CASTNet sites with positive differences are located in the southern states. The remaining eastern sites recorded below-normal precipitation as did most of the western sites.

The fourth highest daily maximum 8-hour O<sub>3</sub> concentrations and SUM06 values (Figures 4-2 and 4-3) observed at CASTNet sites in the eastern United States show a rough geographic correlation with the patterns of temperature and solar radiation differences. However, western measurements of fourth highest daily maximum 8-hour O<sub>3</sub> levels and SUM06 were generally lower in 2001, especially along the continental divide, despite warmer, sunnier, and drier weather.

# **Evaluation of One-Hour and Eight-Hour Concentrations**

Although CASTNet is a non-urban, largely rural network, several sites exceeded the 1-hour NAAQS, which permits up to three 1-hour averages at or above 125 ppb over a 3-year period. Table 4-1 shows the sites that observed O<sub>3</sub> levels above 125 ppb for the five 3-year periods between 1995 and 2001.

The site located at Beltsville, MD (BEL116) consistently observed more than three days in each 3-year period with hourly O<sub>3</sub> levels at or above 125 ppb. BEL116, which is affected by transportation, utility, and commercial emissions in the metropolitan Washington, DC area, observed O<sub>3</sub> levels at or above 125 ppb for four or more days per 3-year period. WSP144, which lies between populated areas of New Jersey and Philadelphia and is similarly affected by pollution from those regions, recorded nine or more high hourly O<sub>3</sub> levels over the most recent 3-year periods. The sites at ABT147, JOT403, and GAS153 also measured ozone levels above the 1-hour NAAQS. ABT147 is downwind of metropolitan New York. JOT403, which encounters transported pollution from the Los Angeles area, consistently observed some of the highest ozone levels in the network. High ozone levels at GAS153 were influenced by Atlanta's air pollution spreading out to surrounding rural areas.

**Table 4-1.** Number of Days at CASTNet Sites with Hourly O<sub>3</sub> Concentrations Greater Than or Equal to 125 ppb over 3-Year Periods

0 / 41 0 1 441 1 411 0410							
Site ID	State	1995-1997	1996-1998	1997-1999	1998-2000	1999-2001	
ABT147	CT	4	-	4	4	6	
BEL116	MD	4	7	11	11	7	
GAS153	GA	4	5	-	5	-	
JOT403	CA	18	23	20	12	-	
WSP144	NJ	-	-	9	9	11	

However, for both JOT403 and GAS153, all measured 1-hour O<sub>3</sub> levels were below 125 ppb during the most recent 3-year period. Of the almost 100 different locations where CASTNet stations have operated during the period from 1990 to 2000, only five sites, or approximately 5 percent of the network locations, measured hourly O<sub>3</sub> levels at or above 125 ppb for more than three days. The five sites in Table 4-1 sometimes showed very high levels of ozone, with all five having had multiple hours greater than 150 ppb. However, if the new 8hour NAAQS, which is based on a 3-year average of the fourth highest daily maximum 8-hour average concentration, were used to evaluate CASTNet data, the percentage of sites exceeding the standard would be much higher.

Under the new 8-hour standard, the 3-year average must not be greater than or equal to 85 ppb. For example, for the period 1998 through 2000, 34 of the 76 sites that were operating (approximately 45 percent) observed O<sub>3</sub> levels above the 8-hour criterion. This percentage of sites is very similar to percentages estimated in previous studies by Chameides et al. (1997) and Saylor et al. (1998). Chameides et al. (1997) considered eastern CASTNet and Southern Oxidants Study - Spatial Ozone Network (SON) sites and found that 41 of 85 (48 percent) would have not met the 8-hour standard based on 1995 data extrapolated to a 3-year period. Saylor et al. (1998) expanded on this work by including rural Aerometric Information Retrieval System (AIRS) sites in addition to CASTNet and SON sites. They estimated between 30 to 50 percent of rural sites would have observed average 8-hour O<sub>3</sub> levels above the standard for the period from 1993 to 1995. The estimated range was

based on their interpretation of the specifics of the 8-hour standard. To gauge any trend in the percentage of CASTNet sites not achieving the 8-hour standard over five periods, 66 sites were identified with valid 3-year averages for every 3-year period since 1995. Table 4-2 shows the 3-year average 8-hour concentrations for all five periods for the selected sites. Grid cells that are shaded indicate that the site observed O<sub>3</sub> levels at or above 85 ppb for that period. For 28 of the 66 sites considered (42 percent), at least half of the periods were above the 8-hour threshold. Less than half of the sites (30 of 66) show no periods with concentrations at or above 85 ppb.

Table 4-3 shows the number and percentage of the 66 selected sites with concentrations above the 8-hour threshold. The lowest percentage occurred during the most recent period. This finding is consistent with the most recent meteorological data shown in the three box plots (Figures 4-8 through 4-10). The two previous periods (1997-1999 and 1998-2000) had the highest percentage of sites above the threshold, again consistent with the meteorological observations. Figure 4-6 shows that 1991 and 1998 were the two highest years of the 12-year record. The lowest 8-hour concentrations were measured during the period from 1992 to 1994.

Table 4-4 lists the sites with at least one occurrence of days with 8-hour O<sub>3</sub> concentrations at or above 85 ppb during each of the last seven years. These data are consistent with the box plot in Figure 4-6. Frequent, high 8-hour O<sub>3</sub> concentrations were observed along the east coast from the Washington, D.C. area into New England and also in southern California.

Over the period 1995 through 2001, elevated hourly O<sub>3</sub> concentrations were observed along the east coast from Maryland to southern Maine. Frequent, high 8-hour concentrations were also observed in that region. During 2001, hourly concentrations exceeded 125 ppb at CASTNet sites in New Jersey and Connecticut. These same sites also experienced fourth highest daily maximum 8-hour concentrations that exceeded 100 ppb.

**Table 4-2.** 3-Year Averages of Fourth Highest Daily Maximum 8-Hour O<sub>3</sub> Average Concentrations for CASTNet Sites\* (Page 1 of 2)

Site ID	State	1995-1997	1996-1998	1997-1999	1998-2000	1999-2001
ABT147	CT	91	90	94	90	95
ALH157	IL	92	91	92	89	86
ANA115	MI	81	82	86	86	87
ARE128	PA	87	90	91	90	88
ASH135	ME	64	62	65	62	64
BBE401	TX MD	67 97	68 97	65 102	66	63 98
BEL116					100	
BFT142	NC	74 89	80 89	83 90	81 91	76
BVL130	IL	96	97			85 98
BWR139	MD			101	100	
CAD150	AR	77	79	84	85	81
CAN407	UT	68	70	70	73	71
CDR119	WV	76	81	84	84	79
CDZ171	KY	82	83	89	89	85
CHA467	AZ	68	68	68	70	70
CKT136	KY	87	88	87	88	83
CND125	NC	85	92	94	93	86
CNT169	WY	69	71	72	74	75
COW137	NC	70	72	75	79	77
CTH110	NY	82	84	84	82	80
CVL151	MS	76	78	82	85	82
DCP114	ОН	87	92	95	96	88
DEV412	CA	74	79	79	80	79
ESP127	TN	78	80	83	82	79
GAS153	GA	93	96	96	99	91
GLR468	MT	47	50	47	51	48
GRB411	NV	71	72	72	73	72
GRC474	AZ	71	72	73	73	72
GTH161	СО	71	72	73	73	73
HOW132	ME	63	63	71	68	69
JOT403	CA	109	112	109	102	92
KEF112	PA	79	81	82	84	83
LAV410	CA	71	72	76	78	77
LRL117	PA	89	87	86	76	72
LYK123	ОН	76	78	89	87	85
MCK131	KY	86	89	91	91	84
MEV405	CO	65	67	66	70	69
MKG113	PA	86	87	87	87	85
MOR409	WA	52	52	51	57	60
NCS415	WA	44	43	43	46	48
OXF122	ОН	86	89	91	91	85
PAR107	WV	77	79	82	83	80
PED108	VA	78	81	86	85	83
PIN414	CA	84	86	82	82	79
PND165	WY	66	69	70	71	71

**Table 4-2.** 3-Year Averages of Fourth Highest Daily Maximum 8-Hour O<sub>3</sub> Average Concentrations for CASTNet Sites\* (Page 2 of 2)

Site ID	State	1995-1997	1996-1998	1997-1999	1998-2000	1999-2001
PNF126	NC	77	81	84	86	83
PRK134	WI	68	67	74	75	77
PSU106	PA	92	89	92	86	87
QAK172	ОН	85	85	93	91	88
ROM406	CO	72	74	74	77	74
SAL133	IN	89	86	86	85	84
SEK402	CA	101	100	102	102	103
SHN418	VA	85	92	96	93	87
SND152	AL	88	89	91	93	89
SPD111	TN	77	80	86	89	84
STK138	IL	81	80	79	80	81
SUM156	FL	71	76	78	79	74
UVL124	MI	85	84	88	83	84
VIN140	IN	84	86	87	86	82
VOY413	MN	66	66	70	68	67
VPI120	VA	79	84	89	89	84
WEL149	MI	83	83	88	88	88
WSP144	NJ	99	95	104	102	104
WST109	NH	64	66	68	66	66
YEL408	WY	61	62	65	67	67
YOS404	CA	79	88	86	88	86

Note: \* values greater than or equal to the standard of 85 ppb are shaded

**Table 4-3.** Number and Percentage of 66 CASTNet Sites With 3-Year 8-Hour O<sub>3</sub> Average Concentrations Greater Than or Equal to 85 ppb

Period	Number of Sites Above Threshold	Percentage of Sites Above Threshold						
1995-1997	23	34.8						
1996-1998	25	37.9						
1997-1999	32	48.5						
1998-2000	33	50.0						
1999-2001	23	34.8						

Eighteen CASTNet sites recorded 3-year averages of fourth highest daily maximum 8-hour O<sub>3</sub> concentrations that were greater than or equal to 85 ppb for every 3-year period over the last seven years. All but one of these sites were located in the eastern United States. The highest 8-hour concentrations measured at the western site, SEK402, typically exceeded 100 ppb each year. Eight-hour O<sub>3</sub> concentrations exceeded 85 ppb on approximately 48 days per year at this site.

**Table 4-4.** Number of Days during the Ozone Season with 8-Hour Average Ozone Concentrations at or above 85 ppb (Page 1 of 2)

Site ID*	1995	1996	1997	1998	1999	2000	2001
ABT147	11	3	11	7	8	5	14
ACA416	-	-	-	4	5	0	9
ACA416 ALH157	13	9	9	10	10	4	2
	2	3	2	5	11	2	4
ANA115	15	8	7	21	8	3	16
ARE128							
BEL116	19	5	20	24	25	8	16
BFT142	0	0	2	6	2	0	0
BVL130	9	8	3	8	8	4	0
BWR139	16	10	25	30	24	10	11
CAD150	1	0	0	4	7	0	0
CDR119	7	1	1	8	8	2	1
CDZ171	0	1	1	11	11	1	0
CKT136	8	5	0	12	16	0	0
CND125	1	7	4	18	1	3	2
CNT169	0	0	0	0	0	2	0
COW137	0	0	0	1	1	2	0
CTH110	3	2	1	5	8	1	3
CVL151	2	0	0	6	16	2	0
DCP114	5	10	5	19	1	4	2
DEV412	0	0	0	1	4	0	2
ESP127	0	1	2	2	2	1	0
GAS153	13	12	6	19	25	7	3
GRS420	-	-	-	35	37	11	4
HOW132	1	0	0	0	1	0	0
HOX148	-	-	-	-	-	-	5
JOT403	27	48	43	19	38	27	1
KEF112	3	1	0	6	1	2	7
LAV410	-	1	0	1	2	0	0
LRL117	7	1	6	5	1	0	0
LYK123	5	0	5	8	8	2	6
MCK131	11	4	3	15	15	2	0
MKG113	9	5	1	11	7	1	10
OXF122	7	5	4	9	15	4	0
PAR107	3	2	1	4	3	3	0
PED108	2	0	2	11	5	0	3
PIN414	3	9	1	5	1	0	2
PNF126	0	0	0	7	4	5	1
PRK134	0	0	0	0	3	0	2
PSU106	6	2	7	4	12	3	7
QAK172	15	2	4	20	12	2	6
ROM406	0	0	0	1	1	2	0
SAL133	10	8	4	3	11	3	3
SEK402	-	-	45	31	73	52	40
SHN418	5	1	6	22	15	1	8
SND152	7	6	2	23	23	5	3
SPD111	3	0	2	8	6	6	2
SLUIII		v	-	0	0	U	

Table 4-4. Number of Days during the Ozone Season with 8-Hour Average Ozone Concentrations at or above 85 ppb (Page 2 of 2)

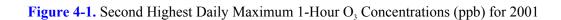
Site ID*	1995	1996	1997	1998	1999	2000	2001
STK138	2	5	0	1	4	0	1
SUM156	0	5	3	2	0	1	0
UVL124	6	6	2	3	11	2	4
VIN140	6	1	3	5	9	3	1
VPI120	1	0	1	12	12	2	1
WEL149	6	3	7	4	12	1	-
WSP144	20	10	1	24	26	12	13
WST109	0	1	3	0	0	0	0
YOS404	-	10	0	9	4	6	4

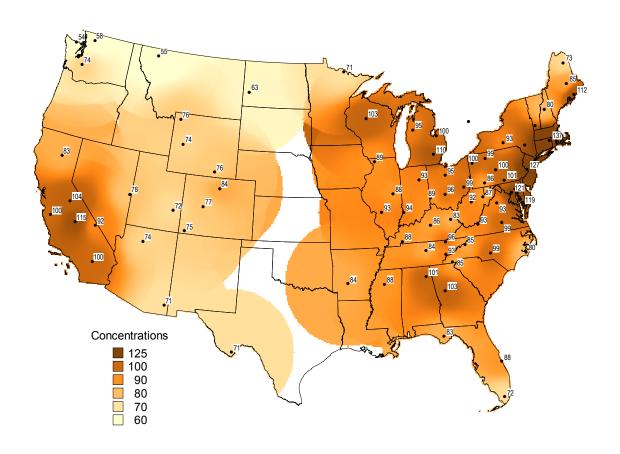
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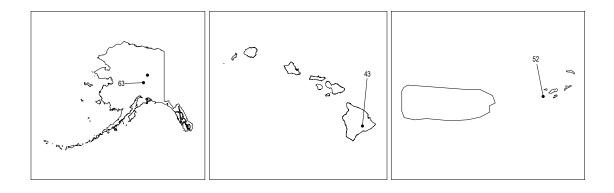
 $\begin{array}{lll} \text{-} & = & \text{no data available (i.e., site not operating)} \\ 0 & = & \text{no days} \geq 85 \text{ ppb} \end{array}$ 

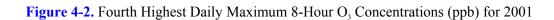
only sites with at least one occurrence during the 6-year period are shown in the table

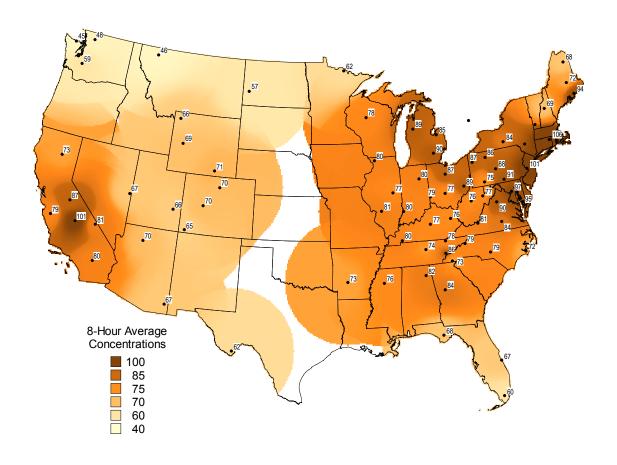
**Note:** In Figures 4-1 through 4-3, the concentration shading was prepared using an algorithm based on inverse distance cubed weighting with a radius of influence of 500 km. Consequently, concentration estimates for areas near the geographic limits of site coverage have no meaning (e.g. western Missouri). Shading was not prepared for Alaska, Hawaii, and the Virgin Islands.











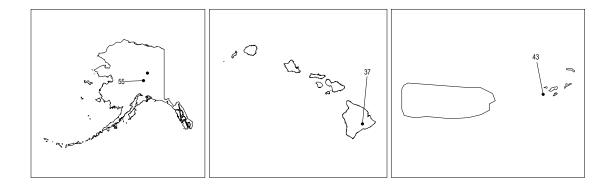
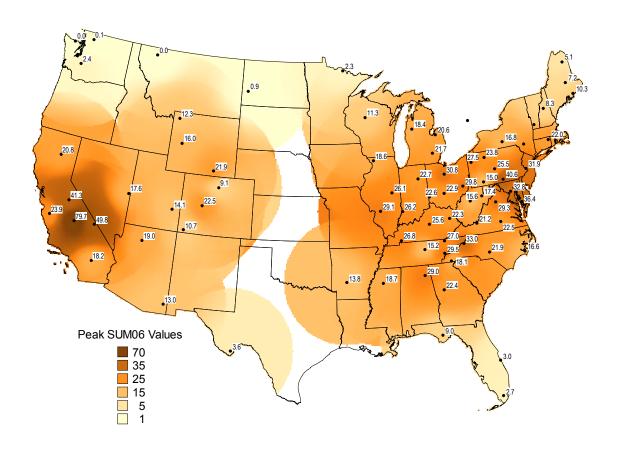


Figure 4-3. Peak SUM06 Values (ppm-hr) for 2001



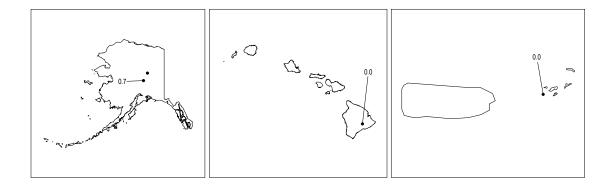
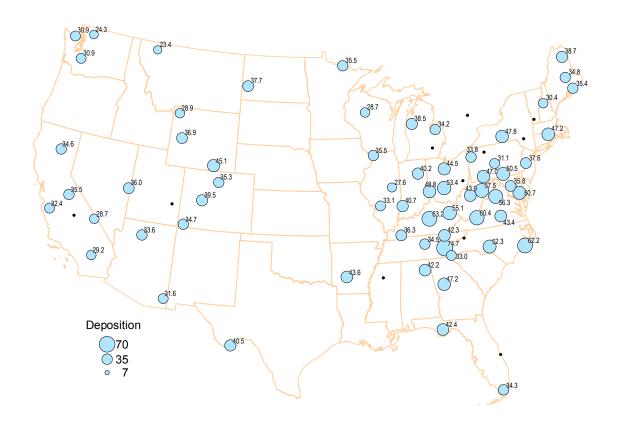
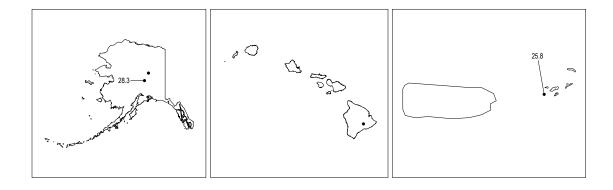


Figure 4-4. Modeled O<sub>3</sub> Dry Deposition Fluxes (kg/ha/yr) for 2001





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Figure 4-5. Trend in Second Highest Daily Maximum 1-Hour O<sub>3</sub> Concentrations (ppb) – Eastern United States

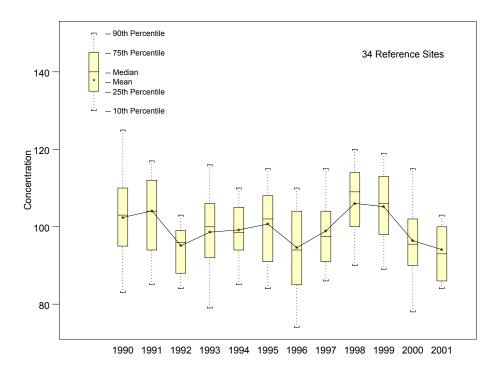
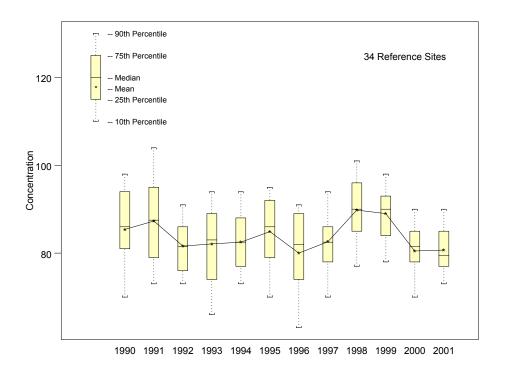
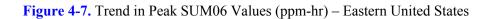


Figure 4-6. Trend in Fourth Highest Daily Maximum 8-Hour O<sub>3</sub> Concentrations (ppb) – Eastern United States





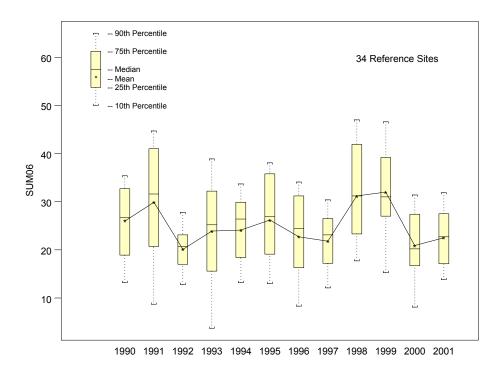
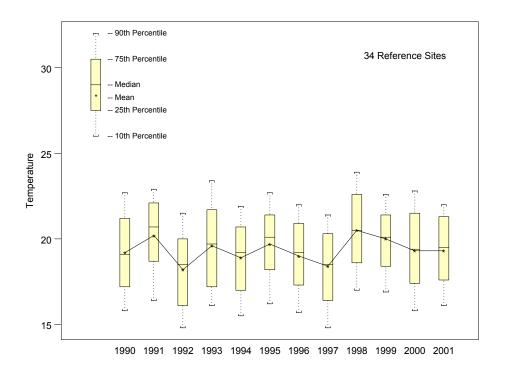
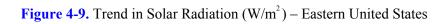


Figure 4-8. Trend in Temperature (°C) – Eastern United States





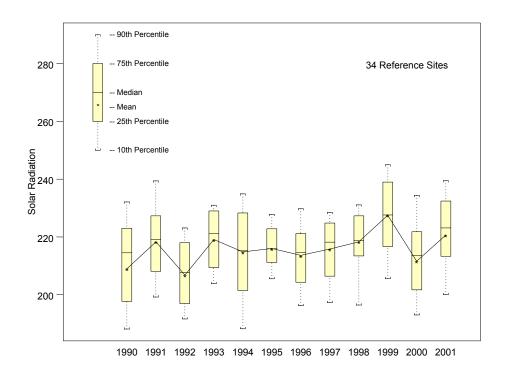
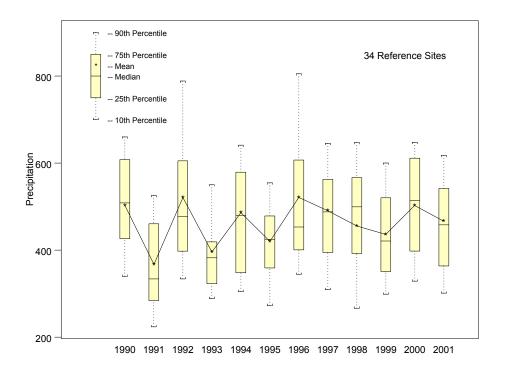


Figure 4-10. Trend in Precipitation (mm) – Eastern United States



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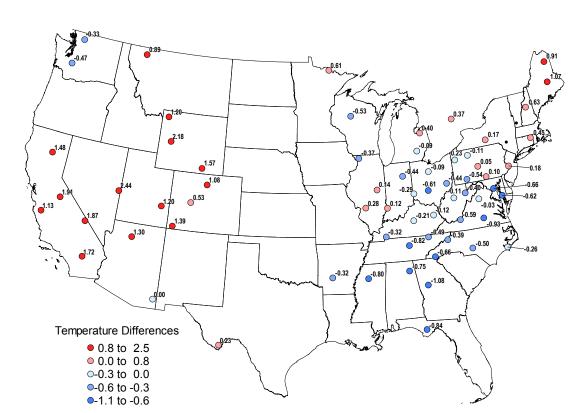
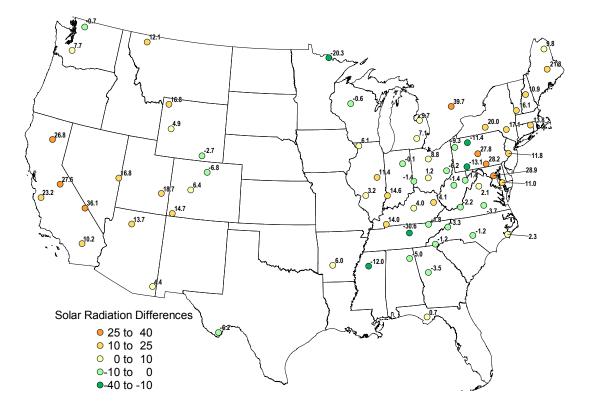
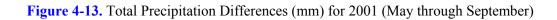
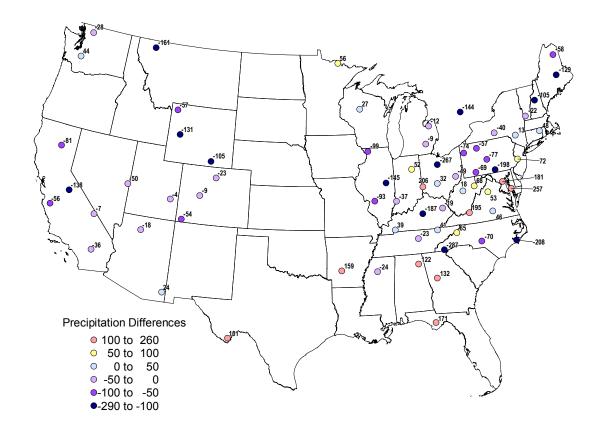


Figure 4-11. Mean Seasonal Temperature Differences (°C) for 2001 (May through September)

Figure 4-12. Mean Seasonal Solar Radiation Differences (W/m<sup>2</sup>) for 2001 (May through September)







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